Thermal Expansion of Rare-Earth-Doped Ceria Ceramics

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希土類固溶セリアの熱膨張

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The thermal expansion of CeO_2 and rare-earth-doped ceria ($\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_{1.9}$, R: Yb, Y, Gd, Sm, Nd and La) was measured in the temperature range from 298 to 1473 K. The coefficients of thermal expansion (CTE) were determined by differentiating the thermal expansion expressed by a polynomial equation of temperature with respect to temperature. The CTE (α_1) for $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_{1.9}$ was in the range from 10×10^{-6} to $14 \times 10^{-6} \text{ K}^{-1}$ and increased nonlinearly with increasing temperature. This result was explained by the asymmetric curve of potential energy based on the lattice energy theory. The kinds of dopant gave small effect on the α_1 of rare-earth-doped ceria. On the other hand, the average CTE for CeO_2 and rare-earth-doped ceria ($12.0\text{--}12.5 \times 10^{-6} \text{ K}^{-1}$), determined from a linear approximation of thermal expansion with respect to temperature at 298–1273 K, was lower than the α_1 and close to the previously reported values.

[Received March 8, 2002; Accepted May 21, 2002]

Key-words: Rare-earth-doped ceria, Coefficient of thermal expansion, Potential energy, Ionic radius, Lattice energy theory

1. Introduction

Solid oxide fuel cell (SOFC) can generate high-efficiency electric power using H_2 and O_2 gases without environmental pollution, noise and vibration. The well used solid electrolyte of SOFC is Y_2O_3 -stabilized ZrO_2 (YSZ). The SOFC system with YSZ is operated at about 1000°C. Reducing the operation temperature is useful in increasing the lifetime and choice of the constituent materials (anode, cathode and interconnector) of SOFC. Rare-earth-doped ceria has a higher oxygen ion conductivity than YSZ and is a candidate electrolyte for the low temperature operation.^{1)–4)} In previous papers,^{5)–9)} we reported the synthesis, sintering and electrical conductivity of rare-earth-doped ceria. In addition to the electrical conductivity, the thermal and mechanical properties of solid electrolyte are important factors to design the structure of SOFC.^{10)–13)} The SOFC is a multilayer device consisting of electrolyte, anode, cathode and interconnector. The coefficients of thermal expansion (CTE) of those constituent materials should be close to prevent exfoliation or cracking during heat-cycle of SOFC. Hayashi et al. reported that (1) CTE of Gd-doped ceria became larger with an increase of Gd content and (2) CTE of ceria became large with the increase of oxygen vacancy.¹⁴⁾ In this paper, coefficients of thermal expansion of rare-earth-doped ceria ceramics were measured at 298–1473 K in air. The lattice energy theory was applied to analyze the effects of temperature and dopant on CTE.

2. Experimental

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (purity > 98.9 mass%), $\text{R}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (purity > 99.5 mass%, R: Yb, Y, Gd, Sm, Nd or La) and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (purity > 99.9 mass%) were used as starting materials.⁵⁾ The cerium and rare-earth nitrate solutions of 0.20 M were mixed at the molar ratio of $\text{Ce}/\text{R}=4/1$. The oxalate coprecipitate was prepared by adding the mixed oxalate solution into a stirred oxalic acid solution of 0.4 M drops by drops. The precipitate produced was vacuum-filtrated, washed with distilled water and decomposed to oxide by calcination at 600°C for 1 h in air. The undoped and rare-earth-doped ceria powders of 41.3 g (40.9 cm^3) were milled with alumina ball (0.3 cm diameter) of 344 g for

24–36 h at a rate of 85 r.p.m in polyethylene container of 280 cm^3 (5.5 cm diameter, 12 cm length). The phases produced in heated oxides were identified by X-ray powder diffraction. The lattice parameters of crushed powders of samples sintered at 1600°C were measured with X-ray powder diffraction (No.2013, Rigaku Co., Tokyo) using NaCl as a standard substance (50 mass%) at a scan speed of $0.5^\circ/\text{min}$.

The calcined powders were consolidated by uniaxial pressing (49 MPa) and subsequent cold isostatic pressing (294 MPa), and sintered at 1600°C for 4 h in air. The bulk density was measured by the Archimedes method using distilled water. Thermal expansion of sintered rectangular sample ($5 \times 5 \times 20 \text{ mm}^3$) polished with abrasive SiC paper No. 1200 was measured with TMA (thermomechanical analyzer; Model 8310, Rigaku Co., Tokyo). The sample was twice heated to 1200°C in air and cooled to room temperature at a heating and cooling rate of $10^\circ\text{C}/\text{min}$. The coefficient of thermal expansion was measured upon the second heating. The measured thermal expansion data were calibrated by blank test and the reference data of α -alumina.

3. Results and discussion

All the samples were sintered above 98% of theoretical density at 1600°C. No crystalline or amorphous secondary phase in the grain interior or at grain boundaries was observed by transmission electron microscopy.⁷⁾ Lattice parameter (a) increased linearly with increasing the ionic radius of the doped rare-earth element and was fitted by Eq. (1) for the composition of $\text{Ce}_{1-x}\text{R}_x\text{O}_{2-(x/2)}$,

$$a = \frac{4}{\sqrt{3}} [xb_1 + (1-x)b_2 + (1-0.25x)b_3 + 0.25xb_4] \times 0.9971 \quad (1)$$

where b_1 , b_2 , b_3 and b_4 are the radii of the cation dopant, cerium ion (0.097 nm), oxygen ion (0.138 nm) and the oxygen vacancy, respectively.^{7),15)} Hong and Virkar¹⁵⁾ proposed a value of 0.1164 nm for b_4 . The correction factor, 0.9971, was introduced from the ratio of the lattice parameter measured for pure ceria (0.5411 nm, JCPDS No. 34-394) to the

Fig. 1. Thermal expansion of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$.

Table 1. Experimental Constants of Thermal Expansion Expressed by $\Delta L/L_1 = c_1 + c_2T + c_3T^2 + c_4T^3$ (L_1 : Initial Length at Room Temperature) in the Temperature Range from 298 to 1473 K and Coefficients of Correlation for CeO_2 and Rare-Earth-Doped Ceria

Sample	c_1	c_2	c_3	c_4	Coefficient of correlation
CeO_2	-0.280	8.11×10^{-4}	3.53×10^{-7}	-7.89×10^{-11}	>0.9999
$\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$	-0.249	6.76×10^{-4}	5.46×10^{-7}	-1.41×10^{-10}	>0.9999
$\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$	-0.262	7.25×10^{-4}	5.21×10^{-7}	-1.44×10^{-10}	>0.9999
$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$	-0.274	7.73×10^{-4}	4.46×10^{-7}	-1.19×10^{-10}	>0.9999
$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$	-0.290	1.03×10^{-3}	8.64×10^{-8}	1.86×10^{-11}	>0.9999
$\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$	-0.296	8.86×10^{-4}	2.54×10^{-7}	-3.68×10^{-11}	>0.9999
$\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$	-0.272	7.78×10^{-4}	3.97×10^{-7}	-9.68×10^{-11}	>0.9999

calculated value 0.5427 nm based on the ionic radii.

Figure 1 shows the thermal expansion ($\Delta L/L_1$, L_1 : initial length at room temperature) of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$. The measurement result was approximated by Eq. (2),

$$\frac{\Delta L}{L_1} = c_1 + c_2T + c_3T^2 + c_4T^3 \quad (2)$$

where c_1 , c_2 , c_3 and c_4 are the experimental constants, and T is temperature (K). As seen in Fig. 1, the data were well fitted by Eq. (2). Table 1 summarizes the c values in Eq. (2) and the coefficients of correlation for all the samples measured. The coefficients of correlation were greater than 0.9999. The c_1 and c_4 were negative values except for the c_4 of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, and the c_2 and c_3 resulted in positive values.

The CTE (α_1) based on the sample length at room temperature (L_1) was determined by differentiating Eq. (2) with respect to T (Eq. (3)).

$$\alpha_1 = \frac{1}{L_1} \left(\frac{dL}{dT} \right) = c_2 + 2c_3T + 3c_4T^2 \quad (3)$$

Figure 2 shows the α_1 of CeO_2 , $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$ as a function of temperature. The α_1 was in the range from 10×10^{-6} to $14 \times 10^{-6} \text{ K}^{-1}$ and increased nonlinearly with increasing temperature. This result is explained by the potential energy curve based on the lattice energy theory. The potential energy between cation and anion is expressed by Eq. (4),

Fig. 2. Coefficients of thermal expansion of CeO_2 , $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$, based on the sample length at room temperature.

$$E = -\frac{AN_A Z_1 Z_2 e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n} \quad (4)$$

where A is the Madelung constant 2.51939 for the fluorite structure, N_A the Avogadro constant 6.022×10^{23} , Z_1 the average cation valence 3.8 ($4(\text{Ce}) \times 0.8 + 3(\text{R}) \times 0.2$), Z_2 the average anion valence including oxygen vacancy 1.9 , e the charge on the electron $1.602 \times 10^{-19} \text{ C}$, B the repulsion coefficient, n the Born exponent 9.5 (12 for Ce^{4+} and R^{3+} , 7 for O^{2-} , $(12+7)/2=9.5$) and ϵ_0 the permittivity of vacuum $8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$. The B value is given by Eq. (5) from the condition, $dE/dr=0$ at $r=r_0$ (the equilibrium distance of the Ce-O bond at 0 K).

$$B = \frac{AN_A Z_1 Z_2 e^2}{4\pi\epsilon_0} \cdot \frac{r_0^n}{n} \quad (5)$$

The thermal expansion of the cation-O bond was assumed to be expressed by Eq. (2). That is, r_0 value is given by Eq. (6),

$$r_0 = (1 + c_1)r_1 \quad (6)$$

where r_1 is the distance of the cation-O bond which was measured as lattice constant at room temperature (Eq. (1)). Figure 3 shows the calculated potential energy curves for $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$. The average distance ($\bar{r}$) of cation-O bond and the temperature corresponding to the thermal expansion based on r_0 are plotted in Fig. 3. The thermal expansion, $(\bar{r} - r_0)/r_0$, becomes larger at higher temperature because of the asymmetric curve of potential energy, explaining the results shown in Fig. 2.

Equation (7) and Fig. 4 show the normalized relation between the potential energy (E/E_0) and distance of cation-O bond (r/r_0) for a rare-earth-doped ceria.

$$\frac{E}{E_0} = \frac{r_0}{r} \cdot \frac{n + \left(\frac{r_0}{r} \right)^{n-1}}{n+1} \quad (7)$$

The normalized potential energy curve is independent of the dopant. The effect of dopant on CTE is reflected in the corresponding temperature, indicating small influence of dopant. These corresponding temperatures in Figs. 3 and 4 were associated with the thermal expansion coefficient calculated by Eq. (8). The CTE (α_0) based on the sample length at 0 K (L_0) is expressed by Eq. (8).

$$\alpha_0 = \frac{1}{L_0} \left(\frac{dL}{dT} \right) = \frac{\alpha_1}{1 + c_1} \quad (8)$$

Figure 5 shows α_0 for the rare-earth-doped ceria and undoped ceria. The difference in α_0 values with the dopant was

Fig. 3. Calculated potential energy curves for $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$.

Fig. 4. Normalized relation between potential energy (E/E_0) and distance of cation-O bond (r/r_0) for rare-earth-doped ceria.

Fig. 5. Coefficients of thermal expansion of CeO_2 , $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$, based on the sample length at 0 K.

less than $0.5 \times 10^{-6} \text{ K}^{-1}$ in the temperature range from 700 to 1500 K, indicating the small influence of dopant. Since the change of sample length with temperature (dL/dT) in Eq. (3) is the same value that in Eq. (8), the α_0 becomes larger than the α_1 because L_0 is shorter than L_1 .

Table 2 compares the α_1 value at 1273 K with the average CTE in the temperature range from 298 to 1273 K for the rare-earth-doped ceria and undoped ceria. The average α_1 (No. 1) in Table 2 corresponds to c_2 in Eq. (3) for $c_3 = c_4 = 0$ when the thermal expansion at 298–1273 K was approximated by a linear relation with respect to temperature using the least-squares method. The average α_1 (No. 2) was calculated from the two sample lengths at 298 and 1273 K. As seen in Table 2, the difference in CTE with the dopant in ceria was small and the CTE value became smaller in the following order: $\alpha_1 > \text{average } \alpha_1 \text{ (No. 1)} \geq \text{average } \alpha_1 \text{ (No. 2)}$. The measured average α_1 (No. 2) was compared with the previously reported ones. Our data were very close to the reference data in Table 2. The average α_1 (No. 2) for $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ of 93% of theoretical density in Ref. 18) was slightly lower than the result in this experiment with sample of 98.3% of theoretical density. This difference in CTE may come from the influence of porosity.

4. Conclusions

The CTE of rare-earth-doped ceria with a composition of $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_{1.9}$ was measured at 298–1473 K in air and analyzed by the lattice energy theory. The CTE (α_1 , 10×10^{-6} –

Table 2. Coefficients of Thermal Expansion (CTE) of CeO_2 and Rare-Earth-Doped Ceria

Sample	CTE ($\times 10^{-6} \text{ K}^{-1}$)			
	This study			Reference data
	α_1 at 1273 K	ave. α_1 (No.1)* 298 – 1273 K	ave. α_1 (No.2)** 298 – 1273 K	ave. α_1 (No.2)** ≈ 300–1273 K
CeO_2	13.3	12.0	11.8	11.8 (Ref.16) ^{#1} , 12.1±0.5 (Ref.17)
$\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$	13.8	12.5	12.3	—
$\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$	13.5	12.5	12.3	—
$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$	13.3	12.3	12.1	11.59 (Ref.18), 11.8 (Ref.19)
$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$	13.4	12.0	12.2	12.2 (Ref.20) ^{#2}
$\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$	13.5	12.1	11.9	—
$\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$	13.2	12.0	11.9	—

*: determined by a linear approximation of thermal expansion with respect to temperature in the range from 298 to 1273 K.

**: determined from the two sample lengths at 298 and 1273 K.

#1: 298 – 1073 K, #2: 293–1223 K

$14 \times 10^{-6} \text{ K}^{-1}$), determined by differentiating the thermal expansion expressed by a polynomial equation of temperature with respect to temperature, became larger at a higher temperature. This result was explained using the asymmetric potential energy curve as a function of distance of cation–O bond. The dopant in ceria provided small effect on CTE. The average CTE (average α_1 (No. 1)) in the temperature range from 298 to 1273 K, which was determined from a linear approximation of the thermal expansion with respect to temperature using the least-squares method, was lower than the α_1 and close to the average α_1 (No. 2) determined from the two sample lengths at 298 and 1273 K. The average α_1 (No. 2) values in this experiment were very close to the previously reported values.

References

- 1) Etsell, T. H. and Flengas, S. N., *Chem. Rev.*, **70**, 339–79 (1970).
- 2) Tuller, H. L. and Nowick, A. S., *J. Electrochem. Soc.*, **122**, 255–59 (1975).
- 3) Kudo, T. and Obayashi, H., *J. Electrochem. Soc.*, **122**, 142–47 (1975).
- 4) Inaba, H. and Tagawa, H., *Solids State Ionics*, **83**, 1–16 (1996).
- 5) Higashi, K., Sonoda, K., Ono, H., Sameshima, S. and Hirata, Y., *J. Mater. Res.*, **14**, 957–67 (1999).
- 6) Hirata, Y., Ono, H., Higashi, K., Sonoda, K., Sameshima, S. and Ikuma, Y., *Ceram. Trans.*, **92**, 137–48 (1999).
- 7) Sameshima, S., Ono, H., Higashi, K. and Hirata, Y., *J. Ceram. Soc. Japan*, **108**, 985–88 (2000).
- 8) Sameshima, S., Ono, H., Higashi, K., Sonoda, K., Hirata, Y. and Ikuma, Y., *J. Ceram. Soc. Japan*, **108**, 1060–66 (2000).
- 9) Sameshima, S., Higashi, K. and Hirata, Y., *J. Ceram. Proc. Res.*, **1**, 27–33 (2000).
- 10) Sameshima, S., Ichikawa, T., Kawaminami, M. and Hirata, Y., *Mater. Chem. and Phys.*, **61**, 31–35 (1999).
- 11) Minh, N. Q., *J. Am. Ceram. Soc.*, **76**, 563–88 (1995).
- 12) Ftios, C., Nauer, M. and Steel, B. C. H., *J. Eur. Ceram. Soc.*, **12**, 267–70 (1993).
- 13) Kim, N., Kim, B. H. and Lee, D., *J. Power Source*, **90**, 139–43 (2000).
- 14) Hayashi, H., Kanoh, M., Quan, C. J., Inaba, H., Wang, S., Dokiya, M. and Tagawa, H., *Solid State Ionics*, **132**, 227–33 (2000).
- 15) Hong, S. J. and Virkar, A. V., *J. Am. Ceram. Soc.*, **78**, 433–39 (1995).
- 16) Shuk, P. and Greenblatt, M., *Solid State Ionics*, **116**, 217–23 (1999).
- 17) Mogensen, M., Sammes, N. M. and Tompsett, G. A., *Solid State Ionics*, **129**, 63–94 (2000).
- 18) Tompsett, G. A., Sammes, N. M. and Yamamoto, O., *J. Am. Ceram. Soc.*, **80**, 3181–86 (1997).
- 19) Yasuda, I. and Hishinuma, M., Proceedings of Fall Meeting of The Ceramic Society of Japan 1996, Kanazawa (1996) p. 233 [in Japanese].
- 20) Eguchi, K., Setoguchi, T., Inoue, T. and Arai, H., *Solid State Ionics*, **52**, 165–72 (1992).